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STUDIES ON LOW-TEMPERATURE LIGNITE TAR
III. STUDY OF LOW-BOILING TAR ACIDS

by

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This paper will describe the analysis of the lignite tar-acid fraction boiling below 235 C to determine the relative amounts of phenol, cresols, xylenols, and ethyl phenols in low-boiling tar acids. Some work has been previously described in the literature with respect to the analysis of alkyl phenols in the range of the low-boiling tar acids. Recently the emphasis has been on gas-phase chromatography or a combination of gas-phase chromatography and infrared.[1, 2, 3, 4]** However, this technique was not available at the time the analysis was needed. Shortly after this work had been completed, a paper by Fair and Friedrich[5] was published concerning the analysis of alkyl phenol mixtures by infrared. The present work differs from that of Fair and Friedrich and other previous work on tar acids[6, 7, 8] in that, by this method, the tar acids are converted into methyl ethers and the analysis carried out on the ethers.

The conversion to methyl ethers minimizes the possibility of ambiguities due to thermal and oxidative effects and has several advantages from an infrared point of view. It eliminates a band-overlap problem encountered with the free acids and gives materials that are liquid at room temperature, eliminating the need for solvents.

Experimental Procedure

A crude distillate was caustic washed, the separated sodium derivatives benzene extracted, and the tar acids then sprung with acid. The reconstituted tar acids were methoxylated according to the method of Rowe and Bannister, et al.[9], and the unconverted portion subjected to a second treatment. The combined yield was 95 per cent. Infrared showed little difference in the two sets of ethers, which indicated that methylation had not concentrated any particular tar-acid ether. The methyl ethers were

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**The superscript numbers refer to literature references listed at end of paper.

combined and fractionally distilled through a Podbielniak Hypercal column at reflux ratios of 20/1 to 40/1 at one atmosphere under nitrogen. Seventy-seven cuts were taken up to the boiling point of 3, 4-xylenol methyl ether, the highest boiling isomer. The boiling points of the cuts were plotted against weight per cent of the charge distilled as shown in Figure 1. Even when the distillation was taken to a point corresponding to ten additional cuts, the residue was still fluid, indicating little polymerization or decomposition. However, the material boiling above Fraction 78 consisted of methyl ethers of tar acids with boiling points above the xylenols.

From the boiling-point curve, cuts were chosen for spot checking by infrared.* At the points on the curve where the boiling point rose sharply, the rise was bracketed by choosing cuts on either side. From the spectra of these cuts, it was determined that cuts in some boiling-point ranges could be recombined for analysis. The first seventeen cuts were anisole (methyl ether of phenol). From the total weight of these cuts, plus a percentage of several following cuts, the per cent of phenol could be easily calculated. Cuts 23 through 53 were combined and analyzed for the three methyl anisole isomers. Cuts 54 through 77, however, necessitated a cut-by-cut analysis for five to six components per cut.

Pure methyl ethers of phenol and the cresols for use as standards were available by direct purchase. Methyl ethers of the xylenols were prepared at Battelle from purchased xylenols. The ethyl phenols had to be both synthesized and methylated at Battelle. For boiling points of the standards, see Table 1.

TABLE 1. ANALYTICAL WAVELENGTHS OF METHYL ETHERS OF LOW-BOILING TAR ACIDS

Methyl Ether	Boiling Range of Known Ethers, C	Analytical Absorption Band, μ	Baseline Used, μ
Methoxybenzene	152-154	14.47	12.52-14.90
2-Methylmethoxybenzene	170-172	14.01	12.52-14.90
4-Methylmethoxybenzene	173-174	12.23	10.70-13.65
3-Methylmethoxybenzene	175-176	14.49	14.20-14.90
2,6-Dimethylmethoxybenzene	181.5-182.5	9.15	7.50-9.25
2-Ethylmethoxybenzene	184.5-185.5	13.30	12.90-13.90
2,5-Dimethylmethoxybenzene	189.5-190.5	8.68 11.85	7.50-9.25 11.15-13.45
2,4-Dimethylmethoxybenzene	190.5-191.0	8.14 13.29	7.50-9.25 13.10-13.70
3-Ethylmethoxybenzene	192.0-193.0	14.41	13.75-14.90
3,5-Dimethylmethoxybenzene	194.5-195.5	9.33	9.20-9.90
4-Ethylmethoxybenzene	195.5-196.0	12.07 8.52	11.15-13.45 7.40-9.20
2,3-Dimethylmethoxybenzene	195.5-196.0	9.02	7.40-10.40
3,4-Dimethylmethoxybenzene	200.5-201.5	8.30	7.40-10.40

*The infrared instrument used for this work was a Perkin-Elmer Model 21 Spectrophotometer with sodium chloride optics.

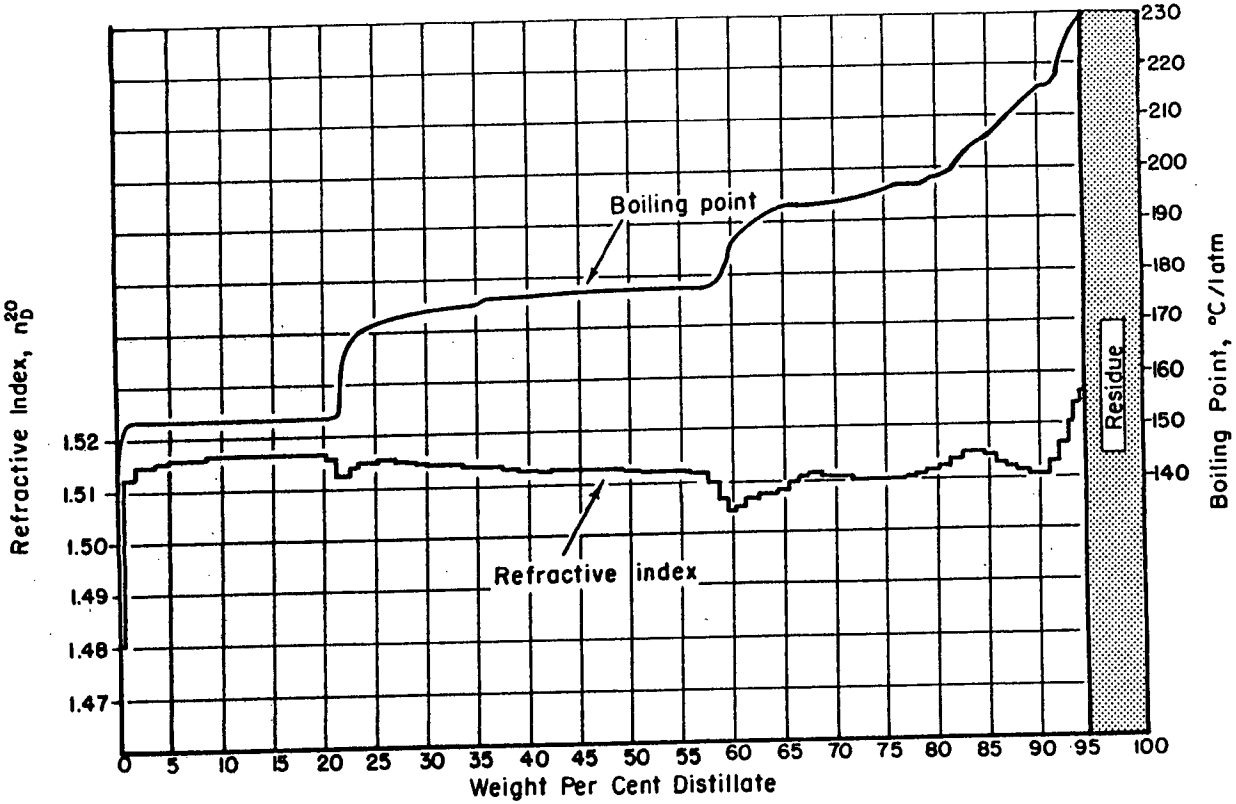

FIGURE 1. FRACTIONATION BY DISTILLATION OF METHYL ETHERS OF LOW-BOILING TAR ACIDS

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Spectra were obtained on the standard methyl ethers in the same cell to be used eventually for the samples. A continuous check was maintained on the cell to make certain no change in cell thickness (0.0053 mm) occurred. From the spectrum of each standard methyl ether, a band (or bands) was selected for measurement of the ether in a mixture. The particular wavelength chosen for measurement was selected on the basis of: (1) minimum interference at that wavelength from absorption due to other ethers which, from boiling points, might reasonably be expected to occur in the same cut; (2) a relatively strong band compared with the rest of the spectrum; and (3) conformance with Beer's law as checked by analysis of synthetic blends. The selected wavelengths for each compound are noted in Table 1.

Band intensities at each selected wavelength in standards and samples were measured by the baseline method. Table 2 gives optical densities of the standards at each selected wavelength. Horizontally, across the table the underlined figure is the optical density in the 0.0053-mm cell of the band chosen for analysis. The other figures indicate the relative amount of interference from the other methyl ethers at the selected wavelength. Percentages of individual components were calculated by solution of simultaneous equations. The method of successive approximation was used.

TABLE 2. ABSORPTION COEFFICIENTS AS MEASURED FROM METHYL-ETHER STANDARDS OF XYLENOLS AND ETHYLPHENOLS

Substituted Methoxybenzene	2,6- Dimethyl	2- Ethyl	2,5- Dimethyl	2,4- Dimethyl	3- Ethyl	3,5- Dimethyl	4- Ethyl	2,3- Dimethyl	3,4- Dimethyl
2,6-Dimethyl	<u>.290</u>	-.002	.003	.000					
2-Ethyl	-.108	<u>.602</u>	-.003	.157	-.115				
2,5-Dimethyl (1)	.011	.020	<u>.470</u>	.100	.420	.124	.006		
(2)		-.068	<u>.103</u>	-.007	.006		.048	-.004	
2,4-Dimethyl (1)	.088	.156	.030	<u>.709</u>	.044	-.002	.220		
(2)			.011	<u>.160</u>	-.022	.004	-.005	-.120	
3-Ethyl		.026	-.002	.000	<u>.310</u>	.044	.035	.000	
3,5-Dimethyl			.005	-.004	.048	<u>.437</u>	.007	-.069	.005
4-Ethyl (1)			.012	.000	-.023	.439	<u>.523</u>		
(2)			.026	.041	.020	.060	<u>.330</u>	-.051	.010
2,3-Dimethyl			.014	.017	.000	-.004	.052	<u>.871</u>	.129
3,4-Dimethyl						-.009	.017	.000	<u>.311</u>

The accuracy for this work is probably about ±10 relative per cent. The accuracy of the analysis could be considerably improved by use of average optical densities obtained from duplicate or triplicate spectra of samples and standards instead of the single determinations used in this case.

Results

Table 3 shows the tar-acid composition based on the analysis as performed on the ethers prepared from lignite tar. By calculation, the primary tar used for this work contained about 0.8 per cent of phenol.

TABLE 3. COMPOSITION OF C_6 THROUGH C_8 TAR ACIDS AS CALCULATED FROM INFRARED ANALYSIS OF THEIR METHYL ETHERS

Compound	Relative Amounts of Isomers of Each Type of Tar Acid, weight per cent		Concentration Per Cent of Each Tar-Acid Isomer in Respect to Total Amount of Tar Acids Identified	
Phenol	100	Phenol	27	
2-Methylphenol	29	Cresols	13	44
3-Methylphenol	39		17	
4-Methylphenol	32		14	
2,3-Dimethylphenol	12	Xylenols	3	18
2,4-Dimethylphenol	32		6	
2,5-Dimethylphenol	19		3	
2,6-Dimethylphenol	5		1	
3,4-Dimethylphenol	14		2	
3,5-Dimethylphenol	18		3	
2-Ethylphenol	17	Ethylphenols	2	11
3-Ethylphenol	32		3	
4-Ethylphenol	51		5	

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